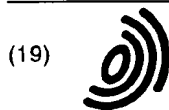


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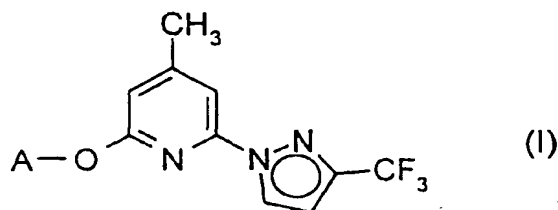
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(54) Herbicidal 2-aryloxy-4-methyl-6-pyrazol-1-yl-pyridines

(57) The novel compounds of formula I:



wherein A has the meaning set forth in the description,
and herbicidal compositions containing such compounds as active ingredients.

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Description

[0001] This invention relates to certain novel 2-aryloxy-4-methyl-6-pyrazol-1-yl-pyridines, to the preparation of such compounds, to herbicidal compositions containing such compounds, and to a method of combating undesired plant growth using such compounds.

[0002] Pyridines and their derivatives have many uses in the pharmaceutical area as well as in agriculture (herbicides, fungicides, acaricides, anthelmintics, bird repellents), as reagents, intermediates and chemicals for the polymer and textile industry.

[0003] The International patent application WO 96/06096 discloses 2-azol-2-yl-5-aryloxy-pyridines in which the azolyl moiety contains at least two heteroatoms in the 1- and 3-position.

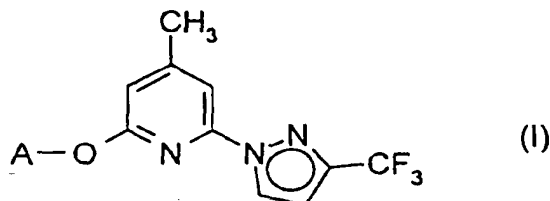
[0004] The broad generic formula of the International patent application WO 98/40379 embraces heteroaryl-(hetero-) aryloxy-pyri(mi)dines in which the heteroaryl moiety is a 5-membered ring is attached to the pyri(mi)dine group via a nitrogen atom of the heteroaryl moiety.

[0005] However, none of these documents discloses 2-(hetero-)aryloxy-4-methyl-6-pyrazol-1-ylpyridines.

[0006] Although many of the known compounds show considerable activity against various weeds, they are not completely satisfying with regard to their selectivity or because of their persistence.

[0007] The compounds according to the present invention combine high herbicidal activity with good selectivity and a desirable rate of degradation in soil.

[0008] The present invention provides novel compounds of the general formula I



wherein

A represents an optionally substituted aryl group or an optionally substituted 5- or 6-membered nitrogen- or sulfur-containing heteroaromatic group or a difluorobenzodioxolyl group; or an agriculturally acceptable salt or N-oxide thereof;

[0009] The new compounds show an excellent selective herbicidal activity in certain crops, such as maize and rice, and degrade well in soil.

[0010] It is an object of the present invention to provide novel herbicidal compounds.

[0011] It is another object of the invention to provide methods for controlling undesired plant growth by contacting said plants with a herbicidally effective amount of the new compounds.

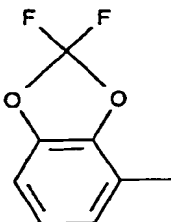
[0012] It is another object of the invention to provide selective herbicidal compositions containing the new compounds as active ingredients.

[0013] These and other objects and features of the invention will become more apparent from the detailed description set forth hereinbelow.

[0014] It has surprisingly been found that the novel compounds of formula I, in which A has the meaning given above, show excellent herbicidal activity against a broad range of weeds and are much more active than those disclosed by the International Patent Application WO 98/40379.

[0015] An aryl group as substituent or part of other substituents or in the definition of A is suitably an optionally substituted phenyl group. Within the definition of A the 5- or 6-membered heteroaryl group comprises optionally substituted 5- or 6-membered heterocycles containing one or more nitrogen and/or oxygen and/or sulfur atoms, 1 to 3 nitrogen atoms being preferred. Examples of such groups are pyrazolyl, imidazolyl, triazolyl, tetrazolyl, thienyl, pyridyl, pyrazinyl, pyrimidyl, pyridazinyl, isoxazolyl, isothiazolyl and triazinyl groups. As far as A is concerned, the definition "aryl" also includes bicyclic systems which consist of a benzene ring fused with a 5- or 6-membered heterocyclic ring as defined above and in turn the 5- or 6-membered heterocycles may be fused with a benzene ring.

[0016] One especially preferred embodiment of the invention is a compound in which A is a difluorobenzodioxolyl group of formula



[0017] A preferably represents a phenyl, pyridyl, thienyl or pyrazolyl group being substituted by one or more of the same or different substituents selected from halogen atoms, alkyl groups, alkoxy groups, cyano groups, haloalkyl groups, haloalkoxy groups, alkylthio groups, haloalkylthio groups and SF₅ groups, and preferably has a substituent in the meta-position relative to the point of attachment; more preferably A is *meta*-substituted by a fluorine or chlorine atom, or a trifluoromethyl, trifluoromethoxy or difluoromethoxy group. If A represents a thienyl group, it may be attached in the 2- or 3-position with respect to the sulfur atom. 3-thienyl groups are preferred.

[0018] Generally, if any of the above mentioned moieties comprises an alkyl, alkenyl or alkynyl group, such groups, unless otherwise specified, may be linear or branched and may contain 1 to 6, preferably 1 to 4, carbon atoms. Examples of such groups are methyl, ethyl, propyl, vinyl, allyl, propargyl, isopropyl, butyl, isobutyl and tertiary-butyl groups. The alkyl portion of a haloalkyl, haloalkoxy, haloalkylthio, alkylthio or alkoxy group suitably has from 1 to 4 carbon atoms, preferably 1 or 2 carbon atoms. The number of carbon atoms in the alkoxyalkyl, alkoxyalkoxy or dialkoxyalkyl groups is up to 6, preferably up to 4, e.g. methoxymethyl, methoxymethoxy, methoxyethyl, ethoxymethyl, ethoxyethoxy, dimethoxymethyl.

[0019] "Halogen" means a fluorine, chlorine, bromine or iodine atom, preferably fluorine, chlorine or bromine. Haloalkyl moieties of any groups within the definitions used herein and as such can contain one or more halogen atoms. Haloalkyl, haloalkoxy and haloalkylthio are preferably mono-, di-, tri- or perfluoroalkyl, -alkoxy and -alkylthio, especially trifluoromethyl, pentafluoroethyl, trifluoromethoxy, difluoromethoxy, difluoromethylthio, trifluoromethylthio or 2,2,2-trifluoroethoxy groups.

[0020] When any groups are designated as being optionally substituted, the optional substituent groups may be any of those customarily employed in the modification and/or development of pesticidal compounds and are especially substituents that maintain or enhance the herbicidal activity associated with the compounds of the present invention, or influence persistence of action, soil or plant penetration, or any other desirable property of such herbicidal compounds.

[0021] There may be one or more of the same or different substituents present in each part of the molecules. In relation to moieties defined above as comprising an optionally substituted alkyl group, including alkyl parts of haloalkyl, alkoxy, alkylthio, haloalkoxy, alkylamino and dialkylamino groups, specific examples of such substituents include phenyl, halogen atoms, nitro, cyano, hydroxyl, C₁₋₄-alkoxy, C₁₋₄-haloalkoxy and C₁₋₄-alkoxycarbonyl groups.

[0022] In relation to moieties defined above as comprising an optionally substituted aryl or heteroaryl group, optional substituents include halogen, especially fluorine, chlorine and bromine atoms, and nitro, cyano, amino, hydroxy, phenoxy, C₁₋₄-alkyl, C₁₋₄-alkoxy, C₁₋₄-haloalkyl, C₁₋₄-haloalkenyl, C₁₋₄-haloalkoxy, C₁₋₄-haloalkylthio, C₁₋₄-alkylsulfonyl and halosulfonyl groups such as SF₅. In the case of phenyl-groups 1 to 5 substituents may suitably be employed, in the case of thienyl-groups 1 to 3 substituents may suitably be employed, 1 or 2 substituents being preferred.

[0023] One skilled in the art will appreciate that not all nitrogen containing heterocycles can form N-oxides; one skilled in the art will recognize those nitrogen atoms which can form N-oxides. Synthetic methods for the preparation of N-oxides of heterocycles are very well known by one skilled in the art including the oxidation of heterocycles with peroxy acids such as peracetic acid and m-chloroperbenzoic acid (MCPBA), hydrogen peroxide, alkylhydroperoxides such as *tert*-butyl hydroperoxide. Such methods for the preparation of N-oxides have been described and reviewed in the literature, as for example: T.L. Gilchrist in *Comprehensive Organic Synthesis*, vol. 7, pp 748-750 and in *Advances in Heterocyclic Chemistry*, vol. 9, pp 285-291, vol. 22, pp 390-392 and vol. 43, pp 149-161, A.R. Katritzky, Ed., Academic Press.

[0024] Compounds of the invention include compounds of formula I, isotopes thereof, geometric and stereoisomers thereof, N-oxides thereof, and agriculturally suitable salts thereof. The compounds of the invention can exist as one or more stereoisomers. The various isotopes include compounds of formula I, in which at least one natural occurring isotope such as a hydrogen or ¹²C carbon atom is replaced by another isotope thereof such as deuterium or ¹³C. The various stereoisomers include enantiomers, diastereomers, atropisomers and geometric isomers. One skilled in the art will appreciate that one stereoisomer may be more active and/or may exhibit beneficial effects when enriched relative to the other stereoisomer(s) or when separated from the other stereoisomer(s). Additionally, the skilled artisan knows how to separate, enrich, and/or selectively prepare said stereoisomers. The compounds of the invention may

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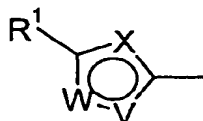
be present as a mixture of stereoisomers, individual stereoisomers, or as an optically active form.

[0025] The salts of the compounds of the invention include acid-addition salts of inorganic and organic acids such as hydrobromic, hydrochloric, nitric, phosphoric, sulfuric, acetic, butyric, fumaric, lactic, maleic, oxalic, propionic salicylic, tartaric, toluenesulfonic or valeric acids.

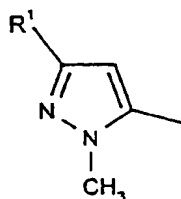
[0026] Preferred compounds of the invention for reasons of better activity and/or ease of manufacture or handling are:

(a) compounds of formula I, wherein A represents a phenyl, pyridyl, pyrazolyl or thienyl group, substituted by one or more of the same or different substituents selected from halogen atoms, alkyl groups, alkoxy groups, cyano groups, haloalkyl groups, haloalkoxy groups, alkylthio groups, haloalkylthio groups.

(b) compounds of formula I, wherein A is a group of formula

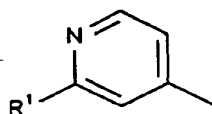


wherein R¹ represents a halogen atom or a haloalkyl or haloalkoxy group W-V represents N-CH, S-CH, N-CH-CH, CH-CH-CH or N-NR²; X represents CH or in the event of W-V being CH-CH-CH also N; and R² represents an alkyl group, in particular wherein R¹ represents a chlorine atom, or a trifluoromethyl, trifluoromethoxy or difluoromethoxy group; most preferably wherein A represents a group of formula a, b, c or d:



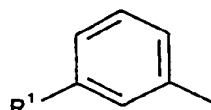
(a)

or



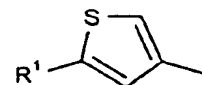
(b)

or



(c)

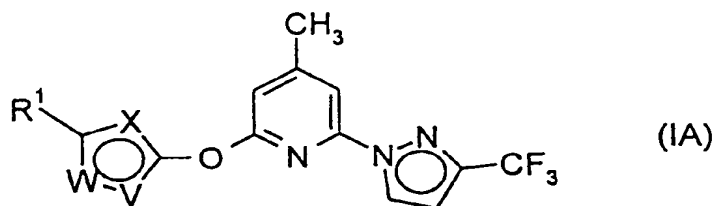
or



(d)

wherein R¹ is a halogen atom or a C₁₋₃ haloalkyl or C₁₋₃ haloalkoxy group, most preferred a chlorine atom, or a trifluoromethyl, pentafluoroethyl, trifluoromethoxy or difluoromethoxy group.

[0027] Particularly preferred are the compounds of formula IA:



(IA)

wherein

R¹ represents a halogen atom or a haloalkyl or haloalkoxy group; W-V represents N-CH, S-CH, N-CH-CH, CH-CH-CH or N-N(CH₃); and X represents CH or in the event of W-V being CH-CH-CH also N.

[0028] The invention is exemplified by the following specific compounds: 2-(2-chloropyrid-4-yloxy)-6-(4'-trifluoromethylpyrazol-1'-yl)-4-methylpyridine, 2-(2-difluoromethoxypyrid-4-yloxy)-6-(4'-trifluoromethylpyrazol-1'-yl)-4-methylpyridine, 2-(1-methyl-3-trifluoromethylpyrazol-5-yloxy)-6-(4'-trifluoromethylpyrazol-1'-yl)-4-methylpyridine, 2-(3-trifluoromethylphenoxy)-6-(4'-trifluoromethylpyrazol-1'-yl)-4-methylpyridine and 2-(2-trifluoromethylpyrid-4-yloxy)-6-(4'-trifluoromethylpyrazol-1'-yl)-4-methylpyridine.

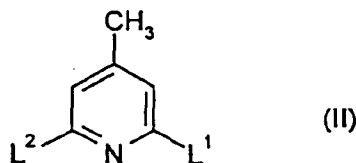
[0029] The compounds of this invention may be oils, gums, or crystalline solid materials. They can be used in agri-

culture or related fields for the control of undesired plants. The compounds of general formula I according to the invention possess a high herbicidal activity within a wide concentration range and at low dosages, and may readily be used in agriculture, especially for the selective control of undesired plants such as *Alopecurus myosuroides*, *Echinochloa crus-galli*, *Setaria viridis*, *Galium aparine*, *Stellaria media*, *Veronica persica*, *Lamium purpureum*, *Viola arvensis*, *Abutilon theophrasti*, *Ipomoea purpurea* and *Amaranthus retroflexus* by pre- and post-emergence application, and particularly in certain crops, such as maize and rice.

[0030] The compounds according to the invention can be prepared by conventional methods as for example disclosed by WO 98/40379, particularly as follows:

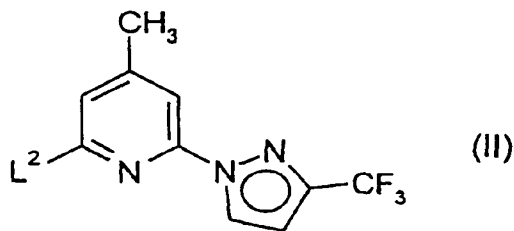
(A) A suitable process for the preparation of the compounds of formula I comprises the steps of:

(a) reacting a respective compound of formula II,



in which L¹ and L² each independently represent a suitable leaving group with 3-(trifluoromethyl)-1H-pyrazole in the presence of a base; and

(b) reacting the resulting compound of formula III

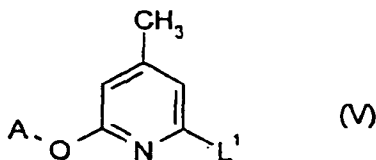


with a compound of formula IV,

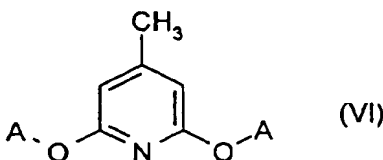


in which A has the same meaning as in formula I, and L² represents a suitable leaving group, in the presence of a base.

(B) Alternatively a compound of formula V:



in which A has the same meaning as in formula I, and L¹ represents a suitable leaving group, is reacted with 3-(trifluoromethyl)-1H-pyrazole in the presence of a base.
(C) Alternatively a compound of formula VI:



10 in which A has the same meaning as in formula I, is reacted with 3-(trifluoromethyl)-1H-pyrazole in the presence of a base.

15 **[0031]** The reactions according to (A) to (C) may be carried out in the absence or presence of a solvent which promotes the reaction or at least does not interfere with it. Preferred are polar, aprotic or protic solvents, suitably being N,N-dimethylformamide, dimethylsulfoxide, sulfolane, acetonitrile, methyl ethyl ketone, or an ether, such as tetrahydrofuran or dioxane, or alcohols, or water, or mixtures thereof. The reactions are carried out at a temperature between ambient temperature and the reflux temperature of the reaction mixture, preferably at elevated temperature, especially at reflux temperature.

[0032] The reactions are as a rule carried out in the presence of a base such as an alkali hydroxide, bicarbonate or carbonate, e. g. sodium or potassium hydroxide, bicarbonate or carbonate, an alkali alkoxide, e. g. sodium ethoxide, an alkali hydride, such as sodium hydride or an organic base such as triethylamine or lithium diisopropylamide.

20 **[0033]** A hydroxy compound used in the above reactions may be present in form of a salt, preferably as a salt of an alkali metal, particularly of sodium or potassium. The presence of a copper salt may be suitable.

[0034] Suitable leaving groups L¹ and L² are each independently e.g. alkyl- and arylsulfonyl groups, alkyl- and arylsulfonyloxy, perfluoroalkylsulfonyloxy groups, and halogen atoms, particularly methanesulfonyl, p-toluenesulfonyl and trifluoromethylsulfonyl groups or fluorine, chlorine and bromine atoms.

25 **[0035]** The compounds used as starting material are known, for example from WO 94/22833.

[0036] The present invention also provides the use of the compounds of formula I as herbicides. Further, in accordance with the invention there is provided a method of combating undesired plant growth at a locus by treating the locus with a composition according to the invention or an effective amount of a compound of formula I. As a useful action is by foliar spray application, the locus is most suitably the plants in a crop area, typical crops being cereals, maize, soya bean, sunflower or cotton. However, application may also be to the soil for those compounds having pre-emergence herbicidal action, or to the water of paddy rice fields. The dosage of active ingredient used may, for example be in the range of from 0.005 to 3 kg/ha, preferably 0.01 to 1 kg/ha.

30 **[0037]** The compounds of general formula I have been found to show interesting activity as herbicides. Accordingly, the invention further provides a herbicidal composition comprising a compound of formula I as defined above in association with at least one carrier, and a method of making such a composition which comprises bringing a compound of formula I into association with at least one carrier. Preferably, there are at least two carriers, at least one of which is a surface-active agent.

40 **[0038]** The invention also provides a method of combating undesired plant growth at a locus, comprising application of such a compound or composition.

[0039] Particularly interesting activity has been found against grasses and broad leaf weeds, pre- and post-emergence. Selectivity in important crop species such as wheat, barley, maize, rice and soya-beans has also been found. This activity provides a further aspect of the present invention.

45 **[0040]** In a method as mentioned above, the dosage of the active ingredient, the compound of general formula I, may, for example, be from 0.005 to 10 kg/ha, suitably 0.01 to 4 kg/ha. The locus may be an agricultural or horticultural locus, comprising, for example, a plant or soil. In a preferred method the locus contains undesired plant growth and treatment is by foliar spray application.

[0041] The invention also provides the use of a compound as defined above, as a herbicide. The compounds of general formula I have been found to have herbicidal activity. Accordingly, the invention further provides a herbicidal composition which comprises an active ingredient, which is at least one compound of formula I as defined above, and one or more carriers. A method of making such a composition is also provided which comprises bringing a compound of formula I as defined above into association with the carrier(s). Such a composition may contain a single active ingredient or a mixture of several active ingredients of the present invention. It is also envisaged that different isomers or mixtures of isomers may have different levels or spectra of activity and thus compositions may comprise individual isomers or mixtures of isomers.

50 **[0042]** A composition according to the invention preferably contains from 0.5% to 95% by weight (w/w) of active ingredient.

[0043] A carrier in a composition according to the invention is any material with which the active ingredient is formu-

lated to facilitate application to the locus to be treated, which may for example be a plant, seed or soil, or to facilitate storage, transport or handling. A carrier may be a solid or a liquid, including material which is normally a gas but which has been compressed to form a liquid.

[0044] The compositions may be manufactured into e.g. emulsion concentrates, solutions, oil in water emulsions, wettable powders, soluble powders, suspension concentrates, dusts, granules, water dispersible granules, micro-capsules, gels and other formulation types by well-established procedures. These procedures include intensive mixing and/or milling of the active ingredients with other substances, such as fillers, solvents, solid carriers, surface active compounds (surfactants), and optionally solid and/or liquid auxiliaries and/or adjuvants. The form of application such as spraying, atomizing, dispersing or pouring may be chosen like the compositions according to the desired objectives and the given circumstances.

[0045] Solvents may be aromatic hydrocarbons, e.g. Solvesso® 200, substituted naphthalenes, phthalic acid esters, such as dibutyl or dioctyl phthalate, aliphatic hydrocarbons, e.g. cyclohexane or paraffins, alcohols and glycols as well as their ethers and esters, e.g. ethanol, ethyleneglycol mono- and dimethyl ether, ketones such as cyclohexanone, strongly polar solvents such as N-methyl-2-pyrrolidone, or γ -butyrolactone, higher alkyl pyrrolidones, e.g. n-octylpyrrolidone or cyclohexylpyrrolidone, epoxidized plant oil esters, e.g. methylated coconut or soybean oil ester and water. Mixtures of different liquids are often suitable.

[0046] Solid carriers, which may be used for dusts, wettable powders, water dispersible granules, or granules, may be mineral fillers, such as calcite, talc, kaolin, montmorillonite or attapulgite. The physical properties may be improved by addition of highly dispersed silica gel or polymers. Carriers for granules may be porous material, e.g. pumice, kaolin, sepiolite, bentonite; non-sorptive carriers may be calcite or sand. Additionally, a multitude of pregranulated inorganic or organic materials may be used, such as dolomite or crushed plant residues.

[0047] Pesticidal compositions are often formulated and transported in a concentrated form which is subsequently diluted by the user before application. The presence of small amounts of a carrier which is a surfactant facilitates this process of dilution. Thus, preferably at least one carrier in a composition according to the invention is a surfactant. For example, the composition may contain at two or more carriers, at least one of which is a surfactant.

[0048] Surfactants may be nonionic, anionic, cationic or zwitterionic substances with good dispersing, emulsifying and wetting properties depending on the nature of the compound according to general formula I to be formulated. Surfactants may also mean mixtures of individual surfactants.

[0049] The compositions of the invention may for example be formulated as wettable powders, water dispersible granules, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates and aerosols. Wettable powders usually contain 5 to 90% w/w of active ingredient and usually contain in addition to solid inert carrier, 3 to 10% w/w of dispersing and wetting agents and, where necessary, 0 to 10% w/w of stabilizer(s) and/or other additives such as penetrants or stickers. Dusts are usually formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant, and may be diluted in the field with further solid carrier to give a composition usually containing 0.5 to 10% w/w of active ingredient. Water dispersible granules and granules are usually prepared to have a size between 0.15 mm and 2.0 mm and may be manufactured by a variety of techniques. Generally, these types of granules will contain 0.5 to 90% w/w active ingredient and 0 to 20% w/w of additives such as stabilizer, surfactants, slow release modifiers and binding agents. The so-called "dry flowables" consist of relatively small granules having a relatively high concentration of active ingredient. Emulsifiable concentrates usually contain, in addition to a solvent or a mixture of solvents, 1 to 80% w/v active ingredient, 2 to 20% w/v emulsifiers and 0 to 20% w/v of other additives such as stabilizers, penetrants and corrosion inhibitors. Suspension concentrates are usually milled so as to obtain a stable, non-sedimenting flowable product and usually contain 5 to 75% w/v active ingredient, 0.5 to 15% w/v of dispersing agents, 0.1 to 10% w/v of suspending agents such as protective colloids and thixotropic agents, 0 to 10% w/v of other additives such as defoamers, corrosion inhibitors, stabilizers, penetrants and stickers, and water or an organic liquid in which the active ingredient is substantially insoluble; certain organic solids or inorganic salts may be present dissolved in the formulation to assist in preventing sedimentation and crystallization or as antifreeze agents for water.

[0050] Aqueous dispersions and emulsions, for example compositions obtained by diluting the formulated product according to the invention with water, also lie within the scope of the invention.

[0051] Of particular interest in enhancing the duration of the protective activity of the compounds of this invention is the use of a carrier which will provide slow release of the pesticidal compounds into the environment of a plant which is to be protected as disclosed for example by U.S. patent no. 5,705,174.

[0052] The biological activity of the active ingredient can also be increased by including an adjuvant in the spray dilution. An adjuvant is defined here as a substance which can increase the biological activity of an active ingredient but is not itself significantly biologically active. The adjuvant can either be included in the formulation as a coformulant or carrier, or can be added to the spray tank together with the formulation containing the active ingredient.

[0053] As a commodity the compositions may preferably be in a concentrated form whereas the end user generally employs diluted compositions. The compositions may be diluted to a concentration down to 0.001% of active ingredient.

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The doses usually are in the range from 0.01 to 10 kg a.i./ha. Examples of formulations according to the invention are:

Emulsion Concentrate (EC)		
5	Active Ingredient	Compound of Example 2
	Emulsifier(s)	Atlox® 4856 B / Atlox® 4858 B ¹⁾ (mixture containing calcium alkyl aryl sulfonate, fatty alcohol ethoxylates and light aromatics / mixture containing calcium alkyl aryl sulfonate, fatty alcohol ethoxylates and light aromatics)
	Solvent	Shellsol® A ²⁾ (mixture of C ₉ - C ₁₀ aromatic hydrocarbons)
10	Suspension Concentrate (SC)	
	Active Ingredient	Compound of Example 2
	Dispersing agent	Soprophor® FL ³⁾ (polyoxyethylene polyaryl phenyl ether phosphate amine salt)
15	Antifoaming agent	Rhodorsil® 422 ³⁾ (nonionic aqueous emulsion of polydimethylsiloxanes)
	Structure agent	Kelzan® S ⁴⁾ (Xanthan gum)
	Antifreezing agent	Propylene glycol
	Biocidal agent	Proxel® ⁵⁾ (aqueous dipropylene glycol solution containing 20% 1,2-benisoctiazolin-3-one)
20	Water	to 1000 ml
Wettable Powder (WP)		
	Active Ingredient	Compound of Example 2
25	Wetting agent	Atlox® 4995 ¹⁾ (polyoxyethylene alkyl ether)
	Dispersing agent	Witcosperse® D-60 ⁶⁾ (mixture of sodium salts of condensed naphthalene sulfonic acid and alkylaryl/polyoxy acetates)
	Carrier / Filler	Kaolin
30	Water Dispersible Granules (WG)	
	Active Ingredient	Compound of Example 2
	Dispersing / Binding agent	Witcosperse® D-450 ⁶⁾ (mixture of sodium salts of condensed naphthalene sulfonic acid and alkyl sulfonates)
35	Wetting agent	Morwet® EFW ⁶⁾ (formaldehyde condensation product)
	Antifoaming agent	Rhodorsil® EP 6703 ³⁾ (encapsulated silicone)
	Disintegrant	Agrimer® ATF ⁷⁾ (cross-linked homopolymer of N-vinyl-2-pyrrolidone)
	Carrier / Filler	Kaolin

¹⁾ available from ICI Surfactants

²⁾ available from Deutsche Shell AG

³⁾ available from Rhone-Poulenc

⁴⁾ available from Kelco Co.

⁵⁾ available from Zeneca

⁶⁾ available from Witco

⁷⁾ available from International Speciality Products

[0054] The compositions of this invention can be applied to the plants or their environment simultaneous with or in succession with other active substances. These other active substances can be either fertilizers, agents which donate trace elements or other preparations which influence plant growth. However, they can also be selective herbicides, insecticides, fungicides, bactericides, nematocides, algicides, molluscicides, rodenticides, virucides, compounds inducing resistance into plants, biological control agents such as viruses, bacteria, nematodes, fungi and other microorganisms, repellents of birds and animals, and plant growth regulators, or mixtures of several of these preparations, if appropriate together with other carrier substances conventionally used in the art of formulation, surfactants or other additives which promote application.

[0055] The active ingredients according to the invention can be employed alone or as formulations in combination with conventional herbicides. Such combinations of at least two herbicides can be included in the formulation or also added in a suitable form with the preparation of the tank mix. For such mixtures at least one of the following known herbicides can be used:

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ametrydione, metabenzthiazuron, metamitron, metribuzin, 2,4-D, 2,4-DB, 2,4-DP, alachlor, alloxymid, asulam, atrazin, bensulfuron, bentazon, bifenox, bromoxynil, butachlor, chloridazon, chlorimuron, chlorpropham, chlorsulfuron, chlortoluron, cinmethylin, clopyralid, cyanazin, cycloate, cycloxydim, dichlobenil, diclofop, eptame, ethiozin, fenoxa-prop, fluazifop, fluometuron, fluridone, fluroxypyr, fomesafen, glyphosate, haloxyfop, hexazinone, imazamethabenz, imazapyr, imazaquin, imazethapyr, ioxynil, isoproturon, lactofen, MCPA, MCPP, mefenacet, metazachlor, metolachlor, metsulfuron, molinate, norflurazon, oryzalin, oxyfluorfen, pendimethalin, picloram, pretilachlor, propachlor, pyridate, quizalofopethyl, sethoxydim, simetryne, terbutryne, thlobencarb, triallate, trifluralin, diflufenican, propanil, triclopyr, dicamba, desmedipham, acetochlor, fluoroglycofen, halosafen, tralkoxydim, amidosulfuron, cinosulfuron, nicosulfuron, pyrazosulfuron, thiameturon, thifensulfuron, triasulfuron, oxasulfuron, azimsulfuron, tribenuron, esprocarb, prosulfo-carb, terbutylazin, benfuresate, clomazone, di-methazone, dithiopyr, isoxaben, quinchlorac, qinmerac, sulfosate, cy-closulfamuron, imazamox, imazamethapyr, flamprop-M-methyl, flamprop-M-isopropyl, picolinafen, fluthiamid, isoxaflu-tole, flurtamone, daimuron, bromobutide, methylidimron, dimethenamid, sulcotrione, sulfentrazone, oxadiargyl, acif-luorfen, cafenstrole, carfentrazone, diuron, glufosinate.

[0056] Mixtures with other active ingredients like fungicides, insecticides, acaricides and nematicides are possible.
[0057] A suitable concentrated formulation containing a compound according to the invention can, for example, consist of 100 g of active ingredient (compound of formula I), 30 g of dispersing agent, 3 g of antifoaming agent, 2 g of structure agent, 50 g of anti-freezing agent, 0.5 g of a biocidal agent and water ad 1000 ml. Prior to use, it is diluted with water to give the desired concentration of active ingredient.

[0058] For a more clear understanding of the invention, specific examples are set forth below. These examples are merely illustrations and are not to be understood as limiting the scope and underlying principles of the invention in any way. Various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the following examples and foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

[0059] The structures of the compounds prepared in the following examples were additionally confirmed by NMR and mass spectrometry.

Example 1

4-methyl-2-(-3-trifluoromethyl-1H-pyrazol-1-yl)-6-(3-trifluoromethyl-phenoxy)-pyridine

1A Preparation of 2-bromo-4-methyl-6-(3-trifluoromethyl-1H-pyrazol-1-yl)-pyridine

[0060] A mixture of 2,6-dibromo-4-methylpyridine (33 mmol, obtained according to the method disclosed by WO 94/22833), 3-trifluoromethyl-1H-pyrazole (21 mmol), potassium carbonate (45 mmol) and N,N-dimethylformamide ((50mL) is heated at 90 °C for 4 hours. The reaction mixture is partitioned between ethyl acetate and water. The separated organic phase is washed with brine, dried over sodium sulfate and evaporated *in vacuo* to provide an oily residue which is purified by flash chromatography. To yield 1.9 g of the title compound.

1B Preparation of 4-methyl-2-(-3-trifluoromethyl-1H-pyrazol-1-yl)-6-(3-trifluoromethyl-phenoxy)-pyridine

[0061] A mixture of 1A (5 mmol), 3-trifluoromethylphenol (6.5 mmol), potassium carbonate (10 mmol) and N,N-dimethylformamide (30 mL) is heated at 120 °C for 10 hours. The reaction mixture is partitioned between ethyl acetate and water. The separated organic phase is washed with brine, dried over sodium sulfate and evaporated *in vacuo* to provide an oily residue which is purified by flash chromatography. To yield 1.9 g of the title compound as an off-white solid.

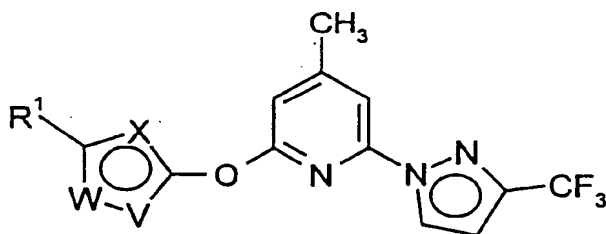
Example 2

4-methyl-2-(-3-trifluoromethyl-1H-pyrazol-1-yl)-6-(1-methyl-3-trifluoromethyl-pyrazol-5-yloxy)-pyridine

[0062] A mixture of 2,6-bis(1-methyl-3-trifluoromethylpyrazol-5-yloxy)-4-methylpyridine (3 mmol, disclosed by WO 94/22833), 3-trifluoromethyl-1H-pyrazole (4 mmol), sodium hydride (4 mmol) and sulfolan (3 mL) is heated at 80 °C for 3 hours. The reaction mixture is partitioned between ethyl acetate and water. The separated organic phase is washed with brine, dried over sodium sulfate and evaporated *in vacuo* to provide an oily residue which is purified by flash chromatography. To yield 300 mg of the title compound, m.p. 101 °C.

Examples 3 to 6:

[0063] Further Examples are prepared according to the general method of Examples 1 and 2 and are listed in Table 1.

Table 1

Example	R ¹	W-V	X
2	Cl	N-CH-CH	CH
3	OCHF ₂	N-CH-CH	CH
4	CF ₃	S-CH	CH
5	CF ₃	N-CH-CH	CH
6	CF ₃	CH-CH-CH	N

Herbicidal Activity

[0064] To evaluate their herbicidal activity, compounds according to the invention are tested using a representative range of plants:

ABUTH	<i>Abutilon theophrasti</i>	velvetweed
AMBEL	<i>Ambrosia artemisiifolia</i>	ragweed
CASOB	<i>Cassia obtusifolia</i>	sicklepod
GALAP	<i>Galium aparine</i>	bedstraw
IPOHE	<i>Ipomoea hederacea</i>	morningglory
LAMPU	<i>Lamium purpureum</i>	deadnettle
MATIN	<i>Matricaria inodora</i>	mayweed
STEME	<i>Stellaria media</i>	chickweed
ALOMY	<i>Alopecurus myosuroides</i>	blackgrass
DIGSA	<i>Digitaria sanguinalis</i>	crabgrass
ECHCG	<i>Echinochloa crus-galli</i>	barnyard grass
LOLMU	<i>Lolium multiflorum</i>	ryegrass
SETVI	<i>Setaria viridis</i>	foxtail
ZEAMX	<i>Zea mays</i>	corn

1. PRE-EMERGENCE TEST

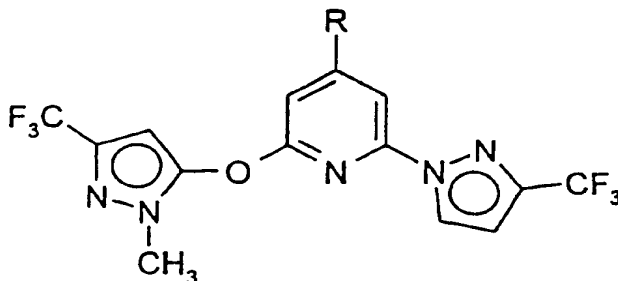
[0065] The pre-emergence tests involve spraying a liquid formulation of the compound onto the soil in which the seeds of the plant species mentioned above has recently been sown.

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[0066] The soil used in the tests is a prepared horticultural loam. The formulations used in the tests are prepared from solutions of the test compounds in acetone containing 0.4% by weight of an alkylphenol/ethylene oxide condensate available under the trade mark TRITON X-155. These acetone solutions are diluted with water and the resulting formulations applied at dosage levels corresponding to 0.013 kg, 0.025 kg, 0.100 kg or 0.400 kg of active material per hectare in a volume equivalent to 900 litres per hectare. In these tests untreated sown soil are used as controls. From 2 to 4 weeks after treatment, the tests are terminated and each pot is examined and rated according to the rating system set forth below:

Rating System	% Difference in Growth Versus Untreated Control
0 - No effect	0
1 - Trace effect	1-5
2 - Slight effect	6-15
3 - Moderate effect	16-29
4 - Injury	30-44
5 - Definite injury	45-64
6 - Herbicidal effect	65-79
7 - Good herbicidal effect	80-90
8 - Approaching complete kill	91-99
9 - Complete kill	100

[0067] The following compounds have been tested:



Compound	R	origin
Example 2	CH ₃	application
Comparison	H	WO 98/40379

[0068] The results of the assessment are set out in Table 2.

Table 2

Assessment (pre-emergence application) 3 weeks after treatment

Compound	Rate [kg/ha]	ABUTH	AMBEL	CASOB	GALAP	IPOHE	LAMPU	MATIN	STEME	ALOMY	DIGSA	ECHCG	LOLMU	SETVI	ZEAMX
Example 2	0.400	9	9	9	8	9	9	9	9	8	9	8	8	9	4
	0.100	8	8	8	6	6	9	9	9	8	9	8	8	9	2
	0.025	3	7	4	3	3	8	8	9	5	9	2	6	9	1
	0.013	1	4	0	1	1	8	7	6	2	9	1	6	9	0
Comparison	0.400	9	8	5	8	7	8	9	9	8	9	7	8	9	2
	0.100	5	6	2	2	3	8	9	8	4	9	4	8	8	1
	0.025	0	4	0	1	1	6	7	8	1	9	2	5	2	0
	0.013	0	0	0	0	0	1	2	0	0	9	0	3	2	0

[0069] Example 2 displayed excellent activity on both broadleaf weeds and grasses. At 0.400 kg/ha all of the thirteen weed species and at 0.100 kg/ha eleven out of thirteen species were well controlled. The weed spectrum controlled included broadleaf weeds such as *Abutilon*, *Ambrosia*, *Cassia*, *Galium*, *Ipomoea*, *Lamium*, *Matricaria*, *Stellaria* and grasses such as *Alopecurus*, *Digitaria*, *Echinochloa*, *Lolium* and *Setaria*. Good selectivity in maize was recorded at 0.100 kg/ha.

[0070] The known compound (Comparison), was clearly inferior in activity to the compound of the invention. At 0.400 kg/ha ten and at 0.100 kg/ha only six out of thirteen species were sufficiently controlled. Accordingly, 0.400 kg/ha of the compound of the prior art were required to obtain the same level of weed control than 0.100 kg/ha of the compound of the invention. Hence, the compound of the prior art required four times more active ingredient for maize selective weed control than the compound of the invention.

2. POST-EMERGENCE TEST

[0071] The post-emergence herbicidal activity of the compounds of the present invention is demonstrated by the following test, wherein a variety of monocotyledonous and dicotyledonous plants are treated with formulations prepared from solutions of the test compounds in acetone containing 0.4 % by weight of an alkylphenol/ethylene oxide condensate available under the trade mark TRITON X-155. These acetone solutions are diluted with water and the resulting formulations applied at dosage levels equivalent of about 0.025 to 0.4 kg per hectare of test compound per pot. After spraying the plants are placed on greenhouse benches and are cared for in the usual manner, commensurate with conventional greenhouse practices. From 2 to 4 weeks after treatment, the seedling plants are examined and rated according to the rating system provided above. The results of the test are set out in Table 3 below.

Table 3

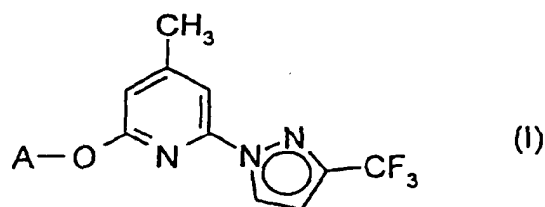
Post-emergence application 2-4 weeks after treatment

Compound	Rate [kg/ha]	ABUTH	AMBEL	CASOB	GALAP	IPHE	LAMPU	MATIN	STEME	ALOMY	DIGSA	ECHCG	LOLMU	SETVI
Example 2	0.400	9	8	9	8	9	9	8	9	8	9	9	9	9
	0.100	8	8	9	6	9	9	8	9	8	8	9	9	8
	0.025	6	6	9	5	9	8	6	8	4	6	6	6	6
Comparison	0.400	8	8	9	8	9	9	8	9	8	8	9	9	8
	0.100	6	6	9	6	9	9	6	9	4	6	7	7	6
	0.025	3	2	9	4	5	7	4	7	2	3	4	4	3

[0072] In post-emergence the compound of the invention displayed again clearly superior activity to the known compound of the prior art. This could be particularly demonstrated at the lower doses of 0.100 and 0.025 kg/ha. At 0.100 kg/ha Example 2 controlled twelve weed species, while Comparison was only active on four species. At 0.025 kg/ha Example 5 controlled still four species compared to only one species sufficiently controlled by the compound of the prior art.

Claims

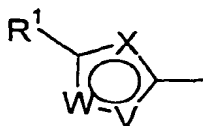
1. A compound of the general formula (I)



wherein

A represents an optionally substituted aryl group or an optionally substituted 5- or 6-membered nitrogen- or sulfur-containing heteroaromatic group or a difluorobenzodioxolyl group;
or an agriculturally acceptable salt or N-oxide thereof;

2. A compound as claimed in claim 1, wherein A represents a phenyl, pyridyl, pyrazolyl or thienyl group, substituted by one or more of the same or different substituents selected from halogen atoms, alkyl groups, alkoxy groups, cyano groups, haloalkyl groups, haloalkoxy groups, alkylthio groups, haloalkylthio groups.
3. A compound as claimed in Claim 3, wherein A is a group of formula

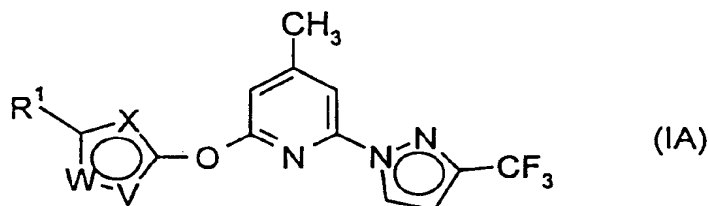


wherein

R¹ represents a halogen atom or a haloalkyl or haloalkoxy group; W-V represents N-CH, S-CH, N-CH-CH, CH-CH-CH or N-NR²; X represents CH or in the event of W-V being CH-CH-CH also N; and R² represents an alkyl group.

4. A compound as claimed in claim 3, wherein R¹ represents a chlorine atom, or a trifluoromethyl, trifluoromethoxy or difluoromethoxy group.

5. A compound of formula IA



wherein

R¹ represents a halogen atom or a haloalkyl or haloalkoxy group; W-V represents N-CH, S-CH, N-CH-CH, CH-CH-CH or N-N(CH₃); and X represents CH or in the event of W-V being CH-CH-CH also N.

6. A compound according to claim 1 selected from the group consisting of

- 2-(2-chloropyrid-4-yloxy)-6-(4'-trifluoromethylpyrazol-1'-yl)-4-methylpyridine,
- 2-(2-difluoromethoxypyrid-4-yloxy)-6-(4'-trifluoromethylpyrazol-1'-yl)-4-methylpyridine,
- 2-(1-methyl-3-trifluoromethylpyrazol-5-yloxy)-6-(4'-trifluoromethylpyrazol-1'-yl)-4-methylpyridine,
- 2-(3-trifluoromethylphenoxy)-6-(4'-trifluoromethylpyrazol-1'-yl)-4-methylpyridine,
- 2-(2-trifluoromethylpyrid-4-yloxy)-6-(4'-trifluoromethylpyrazol-1'-yl)-4-methylpyridine.

7. A herbicidal composition comprising a herbicidally effective amount of at least one compound of formula I, as claimed in claim 1, together with an agronomically acceptable carrier.

8. A composition as claimed in claim 7, comprising at least two carriers, at least one of which is a surface-active agent.

9. A method of combating undesired plant growth at a locus, comprising application to the locus of a herbicidally effective amount of a compound of formula I, as claimed in claim 1.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 00 12 5058

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D, Y	WO 98 40379 A (E.I. DU PONT DE NEMOURS AND CO., USA) 17 September 1998 (1998-09-17) * page 13, table 1, ex. 1 * * page 14, table 1, ex. 11 * * page 19, table 2, ex. 13 * * page 25, table 5, ex. 7 * * Index table A, ex. 1 *	1-7	C07D401/04 C07D417/14 C07D401/14 A01N43/56
Y	DE 197 40 898 A (AMERICAN CYANAMID CO) 26 March 1998 (1998-03-26) * example 2 *	1-7	
A	WO 94 22833 A (SHELL INT RESEARCH ;KLEEMANN AXEL (DE)) 13 October 1994 (1994-10-13) * examples 5,7 *	1-7	
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			C07D A01N
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 January 2001	Examiner Seitner, I
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